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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Gasoline Composition

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(57) 10 Claims

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Notice: This application is as filed and may therefore contain an incomplete specification.

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ABSTRACT

GASOLINE COMPOSITION

The invention provides a gasoline composition comprising a major amount of a gasoline and a minor amount of a mixture of (a) from 75 ppmw to 450 ppmw of a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic 5 compound wherein the alkyl group has a number average molecular weight from 600 to 3000, (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10; and (b) from 75 ppmw to 175 ppmw of an oil-soluble 10 poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the mixture is at least 0.43, all amounts (ppmw) being based on the gasoline composition; a gasoline additive concentrate for use in preparing said composition; and a method of operating a spark-ignition 15 internal combustion engine using said composition.

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GASOLINE COMPOSITION

The present invention relates to a gasoline composition, a gasoline additive concentrate for use in preparing the gasoline composition and a method of operating a spark-ignition internal combustion engine using the gasoline composition.

5 Gasoline compositions have traditionally been formulated to improve the performance of carburetor and throttle body injected engines. Beginning in about 1984, electronic port fuel injected engines were commonly introduced by automobile manufacturers. Shortly thereafter, in about 1985, problems began to be reported 10 with intake valve deposits in electronic port fuel injected engines, which problems are characterized by hard starting, stalls, and stumbles during acceleration and rough engine idle.

Accordingly, it would be desirable to have fuel compositions which reduce or eliminate such undesirable intake valve deposits in 15 electronic port fuel injected engines. Also, since some carburetor and throttle body injector engines will still be in use for the foreseeable future, it would be desirable if such fuels could also be compatible with these engines.

Condensation products of a hydroxyaromatic compound, an 20 amine, and an aldehyde are known to improve detergent properties of fuels used in carburetor and throttle body type engines. U.S. Patent No. 4,231,759 teaches the use of the condensation product of a hydroxyaromatic compound, an amine, and an aldehyde in a carrier 25 of polyolefin, mineral oil, or phenol compounds for removing and preventing deposits on carburetor surfaces and intake valves.

Such compositions have reduced effectiveness in electronic port fuel injected engines where the carrier appears to act like a diluent, reducing the effectiveness of the detergent which it had enhanced in carbureted engines.

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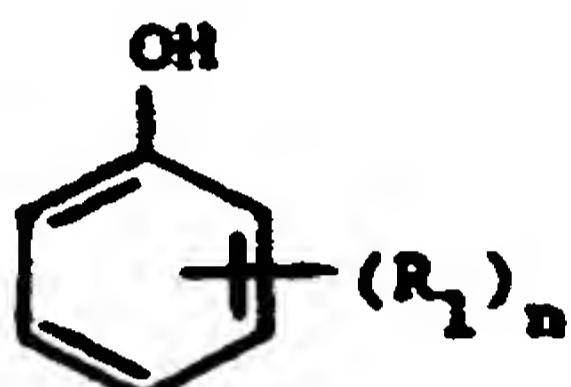
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U.S. Patent No. 4,116,644 discloses a concentrate for use in liquid hydrocarbon fuel boiling in the gasoline boiling range containing

5 (I) as detergent additive, from about 35 to about 50 weight percent of the reaction product of:

(A) one mole part of an alkylphenol having the formula:

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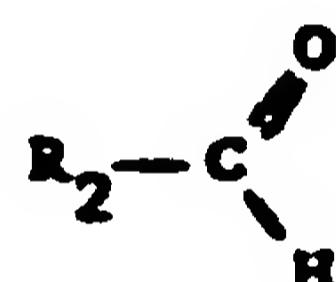


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wherein n is an integer from 1 to 2, and R₁ is an aliphatic hydrocarbon radical having an average molecular weight of from about 400 to 1500;

20 (B) from 1-5 mole parts of an aldehyde having the formula:

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wherein R₂ is selected from hydrogen and alkyl radicals containing 1-6 carbon atoms; and

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(C) from 0.5-5 mole parts of an amine having at least one active hydrogen atom bonded to an amino nitrogen atom, and

(II) from about 1.4 to about 5.6 weight percent of a demulsifying agent containing:

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(A) at least one oil-soluble amine, ammonium, alkaline earth metal, or alkali metal salt of an aryl sulfonic acid;

(B) at least one oil-soluble polyether characterized by the presence within its structure of a group of the formula:



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wherein A is an alkylene group containing from 2 to about 7 carbon

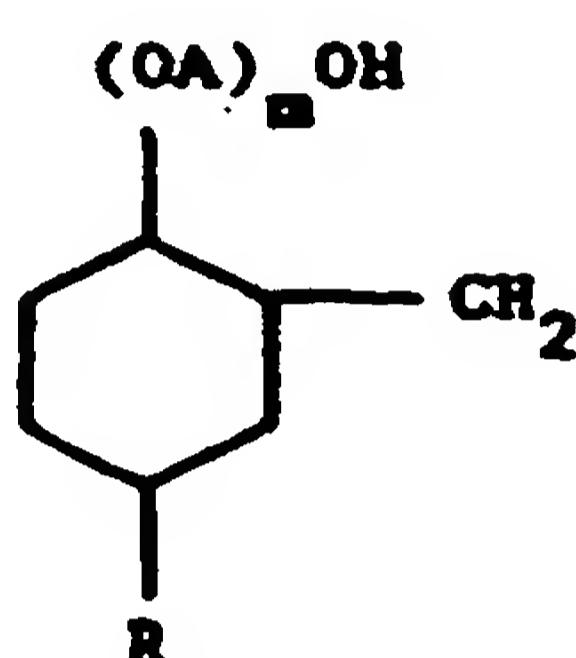
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atoms and where x has an average value of from about 5 to about 200; and

(C) an oxyalkylated phenol formaldehyde resin of the formula:

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wherein A represents an alkylene group containing from about 2 to about 10 carbon atoms, where m has an average value of from about 4 to about 200, and where R is an alkyl group of about from 1 to about 20 carbon atoms.

(III) from about 20 to about 25 weight percent of a mononuclear or dinuclear aromatic hydrocarbon solvent,

(IV) from about 20 to about 35 weight percent of an alkanol having from 4 to 10 carbon atoms, and

(V) from about 3 to about 5 weight percent of a corrosion inhibitor.

The demulsifying agent may contain from about 2 to about 10 parts by weight of aryl sulfonate, from about 0.25 to about 4 parts by weight of polyether glycol, and from about 0.25 to about 4 parts by weight of oxyalkylated phenol formaldehyde resin.

The amount of detergent additive added to the gasoline is said to be in the range from about 3 to 2000 ppm. The amount of demulsifying agent added to the gasoline is said to be dependent, to a degree, upon the concentration of the detergent additive in the gasoline. From about 0.02 to 0.25 ppm of demulsifying agent are added for every one ppm of detergent additive.

Gasolines containing the concentrate are indicated to be advantageous on the basis that they do not suffer from water/gasoline emulsion problems.

35 U.S. Patent No. 4,398,921 discloses a fuel comprising a major

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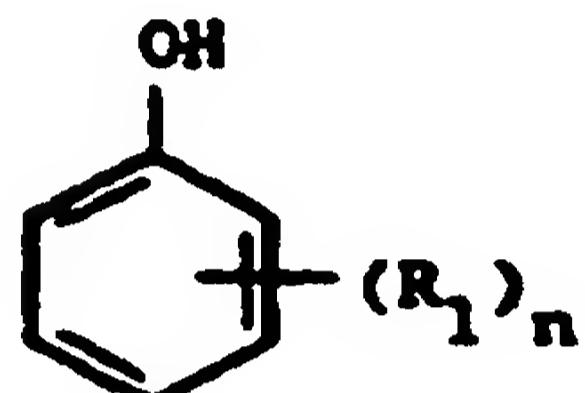
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amount of gasoline, a minor amount of ethanol and a detergent amount (about 1.0 to about 100 ppm) of an additive composition comprising:

5 (I) from about 20 to about 40 weight percent of the reaction product of:

(A) one mole part of an alkylphenol having the formula:

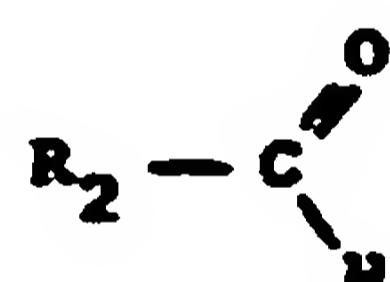
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wherein n is an integer from 1 to 2, and R₁ is an aliphatic hydrocarbon radical having an average molecular weight of from about 400 to 1500;

15 (B) from 1-5 mole parts of an aldehyde having the formula:

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wherein R₂ is selected from hydrogen and alkyl radicals containing 1-6 carbon atoms; and

(C) from 0.5-5 mole parts of an amine having at least one active hydrogen atom bonded to an amino nitrogen atom, and

25 (II) from about 3.0 to about 6.0 weight percent of a demulsifying agent containing:

(A) at least one oil-soluble polyether characterized by the presence within its structure of a group of the formula:

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wherein A is an alkylene group containing from 2 to about 7 carbon atoms and where x has an average value of from about 5 to about 200; and

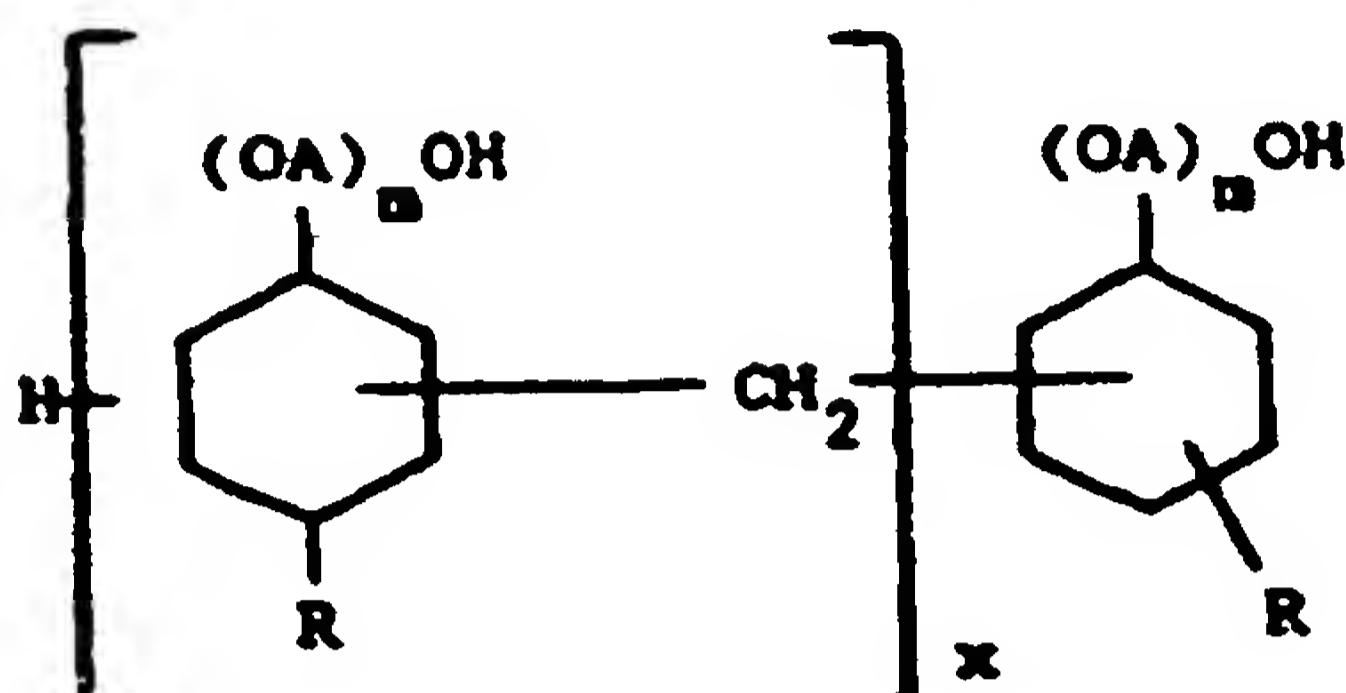
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(B) an oxyalkylated phenol formaldehyde resin of the formula:

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wherein A represents an alkylene group containing from about 2 to about 10 carbon atoms, where n has an average value of from about 4 to about 200, and where R is an alkyl group from about 1 to about 20 carbon atoms, and x is an integer greater than 1.

(III) from about 40 to about 70 weight percent of a mononuclear or dinuclear aromatic hydrocarbon solvent, and

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(IV) from about 5.0 to about 15.0 weight percent of a corrosion inhibitor selected from a hydrocarbyl succinic acid or anhydride having from 12 to 30 carbon atoms (50% in oil).

Such fuels are indicated to be advantageous on the basis that they do not suffer from water/gasoline emulsion problems.

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In accordance with the present invention, there is provided a gasoline composition comprising a major amount of a gasoline and a minor amount of a mixture of (a) from 75 ppmw to 450 ppmw of a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight from 600 to 3000, (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10; and (b) from 75 ppmw to 175 ppmw of an oil soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the mixture is at least 0.43, all amounts (ppmw) being based on the gasoline composition.

The condensation product is prepared by condensing in the usual manner under Mannich reaction conditions: (1) an alkyl-substituted hydroxyaromatic compound, whose alkyl-substituent

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has a number average molecular weight in the range from 600 to 3000, preferably from 750 to 1200, e.g. a polyalkylphenol whose polyalkyl substituent is derived from 1-mono-olefin polymers having number average molecular weight from 600 to 3000, preferably from 750 to 1200; (2) an amine containing at least one $>\text{NH}$ group, preferably an alkylene polyamine of the formula $\text{NH}_2\text{-}(\text{A-NH})_x\text{-H}$ wherein A is a divalent alkylene radical having 2 to 6 carbon atoms and x is an integer from 1 to 10; a particularly preferred amine being one selected from the group consisting of dimethylamine, 10 dimethylaminopropylamine, tetraethylenepentamine, triethylenetetramine, diethylenetriamine and admixtures thereof; and (3) an aldehyde, preferably an aldehyde selected from the group consisting of formaldehyde, paraformaldehyde and admixtures thereof. The condensation product and its preparation are 15 described in further detail in U.S. Patent No. 4,231,759. The amount of condensation product used in the gasoline will be in the range from 75 ppmw up to 450 ppmw, preferably up to 400 ppmw, more preferably up to 250 ppmw, and especially up to 200 ppmw. Highly effective results have been realized when the condensation product 20 is present in 140 ppmw to 180 ppmw, especially 170 ppmw. The ratio of (a) to (b) is at least 0.43, preferably in the range from 0.8 to 1.4, and is especially in the range from 1.2 to 1.4.

Component (b) can be a carrier for component (a) but its presence also aids the effectiveness of the gasoline for control of 25 deposits and engine operation and helps prevent low temperature intake valve sticking. Component (b) is used at concentrations from 75 ppmw up to 175 ppmw, preferably up to 150 ppmw, and especially up to 125 ppmw.

The polymeric carrier used in the present invention, i.e., the 30 oil soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, is well known in the art.

Component (b) is preferably a polyoxyalkylene compound of the formula $\text{R}_1\text{-O-}(\text{R}_2\text{O})_n\text{-R}_3$ wherein each of R_1 and R_3 independently represents a hydrogen atom or an aliphatic, 35 cycloaliphatic or aromatic hydrocarbon radical containing up to 40

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carbon atoms, R_2 represents an alkylene radical containing up to 12 carbon atoms, and n represents an integer of at least 7, preferably at least 20 when R_2O is a 1,2-propyleneoxy group. In the polyoxyalkylene chain - $(R_2O)_n$ - the group R_2 can be any alkylene group. The polyoxyalkylene chain can contain two or more dissimilar alkyleneoxy groups, preferably an alkyleneoxy group of 2 to 8 carbon atoms, especially an ethyleneoxy or 1,2-propyleneoxy group. These groups can be distributed randomly throughout the chain or can be arranged in a pre-determined pattern of units or blocks, each containing one or a plurality of alkyleneoxy groups.

In one embodiment of the invention, at least one of R_1 and R_3 is an alkyl or alkylphenyl group containing up to 20 carbon atoms, for example, a propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, octylphenyl or nonylphenyl group. Preferably, R_1 is hydrogen and R_3 is an alkyl group, more preferably, R_3 is a dodecyl group or a mixture of C_{12} - C_{15} alkyl groups.

Suitable carriers include polyoxypropylene glycols and the glycols containing both ethyleneoxy and 1,2-propyleneoxy groups in the polyoxyalkylene chain as well as the mono- and di-alkyl ethers of such glycols.

The commercially available polyoxyalkylene compounds are generally mixtures of compounds in which the values for n and the molecular weight of such mixtures being only average values. The values of n of typical compounds are usually between 7 and 100, preferably between 8 and 80. The molecular weights vary from 400 to 6000, preferably from 500 to 4000 and more preferably from 1000 to 2000.

The gasoline composition according to the invention comprises a major amount of a gasoline (base fuel) suitable for use in internal combustion engines. This includes hydrocarbon base fuels boiling essentially in the gasoline boiling range from 25°C (77°F) to 232°C (450°F). These base fuels may comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferably the base fuel has a saturated hydrocarbon content in the range from 40 to 80 percent volume, an olefinic

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hydrocarbon content in the range from 0 to 30 percent volume and an aromatic hydrocarbon content in the range from 10 to 60 percent volume. The base fuel can be derived from straight run gasoline, polymer gasoline, natural gasoline, dimer or trimerized olefins, synthetically produced aromatic hydrocarbon mixtures from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, or mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. The octane level, (R+M)/2, will generally be above 85. Any conventional motor base fuel may be employed in the practice of this invention. Thus, in the gasoline, hydrocarbons can be replaced by up to substantial amounts of conventional alcohols, or ethers, conventionally known for use in fuels. The base fuels are desirably substantially free of water. since water may impede a smooth combustion.

Preferably, the gasolines used in the present invention are lead-free, but may contain minor amounts of blending agents such as methanol, ethanol and methyl tertiary butyl ether at from 0.1 to 15% volume of the base fuel. The gasolines can also contain antioxidants such as between 1 ppmw and 40 ppmw phenolics, e.g., 2,6-di-tert-butylphenol or phenylenediamines, e.g., N,N'-di-sec-butyl-p-phenylenediamine; dyes; metal deactivators; dehazers such as polyester-type ethoxylated alkylphenol-formaldehyde resins; corrosion inhibitors, such as a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 500 carbon atoms, for example, pentaerythritol diester of polyisobutylene-substituted succinic acid, the polyisobutylene group having a number average molecular weight of 950, in an amount of 1 to 1000 ppmw; and antiknock compounds such as methyl cyclopentadienylmanganese tricarbonyl or ortho-azidophenol.

The additive mixture (a) plus (b) used in the present invention can be introduced into the combustion zone of the engine in a variety of ways to prevent buildup of deposits, or to

accomplish reduction or modification of deposits. Thus, the additive mixture can be injected into the intake manifold intermittently or substantially continuously, preferably in a hydrocarbon carrier having a final boiling point (by ASTM D86) 5 lower than 232°C (450°F). A preferred method is to add the additive mixture to the gasoline. For example, the additive mixture can be added separately to the gasoline or blended with other gasoline additives.

Accordingly, the present invention further provides a gasoline 10 additive concentrate comprising a major amount of a mixture of (a) from 75 pbw (parts by weight) to 450 pbw of a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number 15 average molecular weight from 600 to 3000, (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants is 1:0.1-10:0.1-10; and (b) from 75 pbw to 175 pbw of an oil soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the 20 mixture is at least 0.43, preferably in the range from 0.8 to 1.4, most preferably in the range from 1.2 to 1.4, and a minor amount of a gasoline compatible diluent, e.g. a gasoline compatible diluent boiling in the range from 50 to 232°C.

Suitable gasoline-compatible diluents are hydrocarbons and 25 mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol or methyl tert-butyl ether. Preferably the diluent is an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol.

30 The present invention still further provides a method of operating a spark-ignition internal combustion engine which comprises introducing to said engine a gasoline composition according to the present invention.

35 The invention will be further understood from the following illustrative example.

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Example

Intake valve detergency is generally defined by the BMW NA standard of intake valve cleanliness for unlimited mileage, which is an established correlation of driveability and intake valve deposit weight of 100 milligrams or less. Intake valve deposit tests were conducted at Southwest Research Institute in 1985 model BMW 318i cars equipped with the 1.8-liter, four-cylinder engine, and were operated for 10,000 miles on the test fuel. Before the test started, deposits were removed from the cylinder head, intake manifold and piston tops and new intake valves were weighed and installed. The oil and filter were changed, new spark plugs installed and the fuel injectors flow checked. Mileage was accumulated on public roads using trained drivers. The test route consisted of about 10% city driving, 20% on secondary roads and 70% highway driving (maximum speed of 65 mph).

The primary test data are the intake valve deposit (IVD) weights at the end of the 10,000-mile test. IVD weights are also determined at 5,000 miles, where tests can be terminated if the results are not promising. BMW's pass criteria are as follows: an average deposit weight of 100 milligrams per valve or less at the conclusion of the test meets BMW requirements for unlimited mileage acceptance; an average deposit weight of 250 mg per valve or less at the conclusion of the test meets BMW requirement for 50,000-mile service.

The Table below lists the additive compositions used in regular unleaded base gasolines and the average intake valve deposit weights at the end of the test (10,000 miles).

Table

Test	Composition			Ratio (a)/(b)	BMW 318i Results Ave. Deposit Weight, mg		
	Component		(a) ppmw				
	(b) ppmw						
1(invention)		170	125	1.36	0		
2		170	125	1.36	46		

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¹ In test 1, "a" is a Mannich condensation product of an alkyl-substituted hydroxyaromatic compound, amine and aldehyde available from Amoco as "Amoco 596" gasoline additive; in test 2, "a" is N-polyisobutetyl-N',N'-dimethyl-1,3-diaminopropane, MW - 5 1050.

² Component "b" is a polyoxypropylene glycol mono ether of a mixed C₁₂-C₁₅ alcohol of average MW 1400.

10 Results of these tests demonstrate that the gasoline composition of the invention (1) passes the BMW unlimited mileage test and had no deposits whereas the other additive package did have deposits.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A gasoline composition comprising a major amount of a gasoline and a minor amount of a mixture of (a) from 75 ppmw to 450 ppmw of a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number average molecular weight from 600 to 3000, (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10; and (b) from 75 ppmw to 175 ppmw of an oil soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the mixture is at least 0.43, all amounts (ppmw) being based on the gasoline composition.
2. A composition according to claim 1, wherein the number average molecular weight of the alkyl substituent is from 750 to 1,200.
3. A composition according to claim 1, wherein the alkyl-substituted hydroxyaromatic compound is an alkyl-substituted phenol.
4. A composition according to claim 1, 2 or 3, wherein the aldehyde is selected from the group consisting of formaldehyde, paraformaldehyde, and admixtures thereof.
5. A composition according to claim 1, 2 or 3, wherein the amine is selected from the group consisting of dimethylamine, dimethylaminopropylamine, tetraethylenepentamine, triethylenetetramine, diethylenetriamine, and admixtures thereof.
6. A composition according to claim 1, 2 or 3, wherein the ratio of (a) to (b) is in the range from 0.8 to 1.4.
7. A gasoline additive concentrate comprising a major amount of a mixture of (a) from 75 pbw to 450 pbw of a condensation product of (1) a high molecular weight sulfur-free alkyl-substituted hydroxyaromatic compound wherein the alkyl group has a number

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average molecular weight from 600 to 3000, (2) an amine which contains an amino group having at least one active hydrogen atom, and (3) an aldehyde, wherein the respective molar ratio of reactants is 1 : 0.1-10 : 0.1-10; and (b) from 75 pbw to 175 pbw of an oil soluble poly(oxyalkylene) alcohol, glycol or polyol or mono or di ether thereof, wherein the weight ratio of (a) to (b) in the mixture is at least 0.43, and a minor amount of a gasoline compatible diluent.

8. A gasoline additive concentrate according to claim 7, wherein the weight ratio of (a) to (b) is in the range from 0.8 to 1.4.

9. A gasoline additive concentrate according to claim 7, wherein the weight ratio of (a) to (b) is in the range from 1.2 to 1.4.

10. A method of operating a spark-ignition-internal combustion engine which comprises introducing to said engine a gasoline composition according to claim 1, 2 or 3.

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